# Discovery of stable quasicrystals by Prof. Tsai and his coworkers

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Currently we look at such classification very naturally.

## Classification of quasicrystals

Crystallographic view point

(1) Rotational symmetry in diffraction
Icosahedral, Octagonal, Decagonal and Dodecagonal

(2) Quasiperiodic translational symmetry (P- and F types)

(3) Atomic cluster
Mackay-, Bergman-, Tsai-types

Component

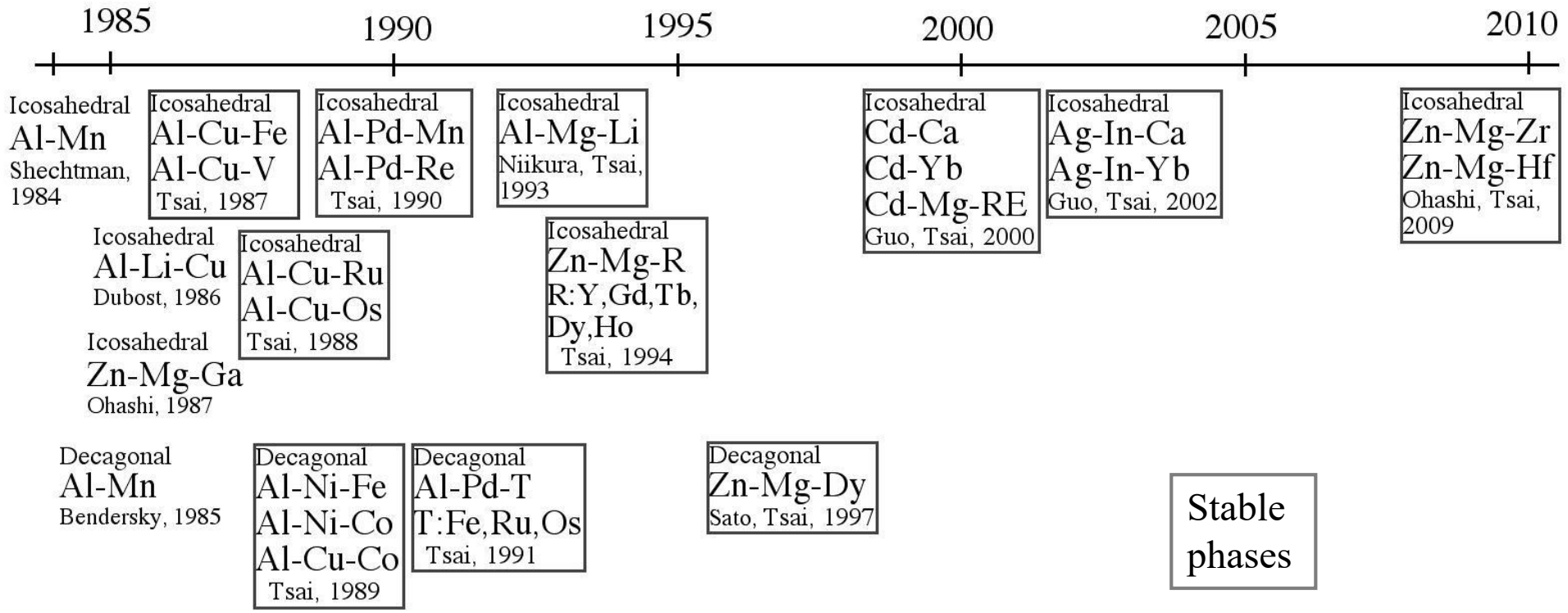
Alloys: Al-, Zn-, Cd-, Ag-, Au-,.... based alloys

Ceramics, Macromolecules, Colloid systems

Surfaces

I like to point out, this owes much to Prof. Tsai's discoveries.

# Chronology of discoveries of stable quasicrystals by Prof. Tsai's group




1st generation: metastable quasicrystals; Al-Mn, Al-Mn-Si
2nd generation: stable but not high quality; Al-Li-Cu, Zn-Mg-Ga
3rd generation: stable and high quality; Al-Cu-Fe, Al-Pd-Mn, Zn-Mg-R
(Almost all discovered by Prof. Tsai's group) Cd-Yb,.....

Prof. Shechtman opened the door,
and Prof. Tsai found many treasure boxes.

# Three types of local structures, namely clusters

Mackay-type
Al-based alloys

Bergman-type
Mainly Zn-based

Tsai-type
Cu-, Zn-, Ag-,
Cd-, Au-,..based

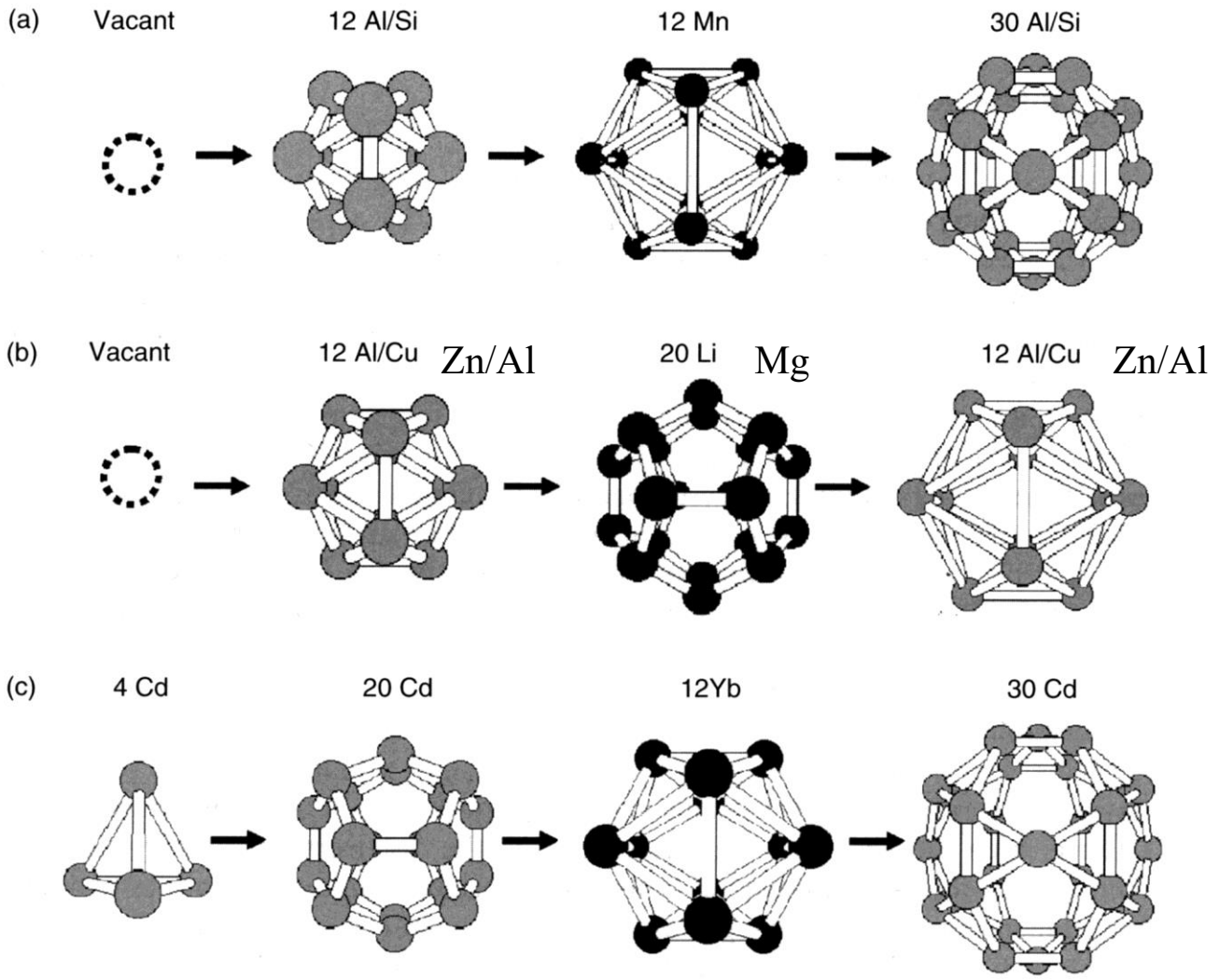


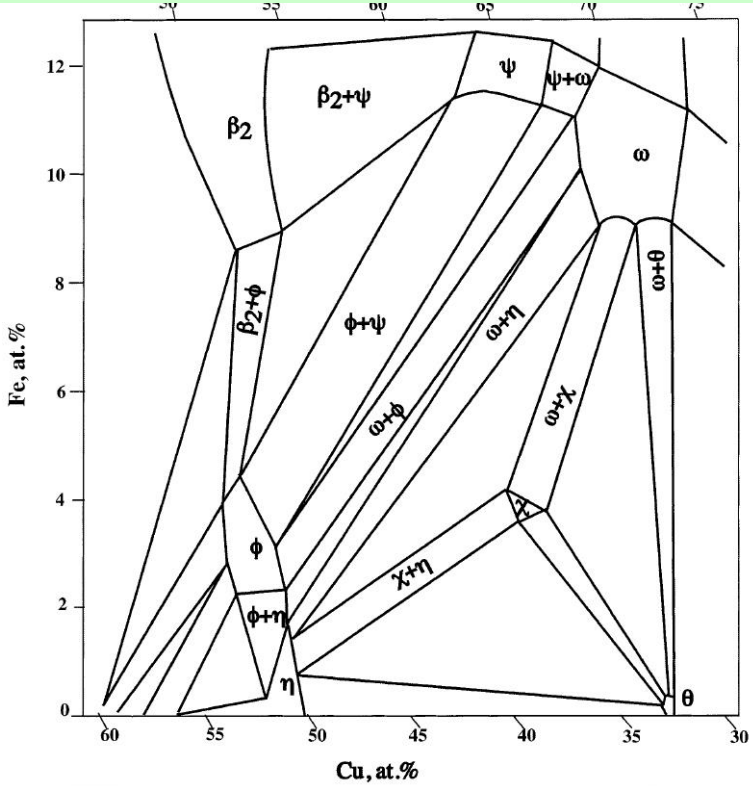

Figure 4.1. Shell structures of three types of icosahedral clusters derived from three 1/1 approximants of quasicrystals. **(a)** The Al–Mn–Si class or Mackay icosahedral cluster: the center is a vacant, 1st shell is a Al/Si icosahedron, 2nd shell is a Mn icosahedrons, and the 3rd shell is a Al/Si icosidodecahedron. **(b)** The Zn–Mg–Al class or Bergman cluster and the example is the R-AlLiCu: the center is a vacant, the 1st shell is a Al/Cu icosahedron, the 2nd shell is a Li dodecahedron, 3rd shell is a larger Al/Cu icosahedron. **(c)** The Cd–Yb class: the center is a Cd tetrahedron, the 1st shell is a Cd dodecahedron, 2nd shell is a Yb icosahedrons, and a 3rd shell is a Cd icosidodecahedron.

Quasicrystals and Approximants in Cd-M Systems and Related Alloys, A.-P. Tsai and C.P. Gomez, in 'QUASICRYSTALS' Handbook of Metal Physics, Edited by T. Fujiwara and Y. Ishii, Elsevier, 2008.

Some of them were already reported as structurely unidentified phases.

## Al-Cu-Fe phase diagram

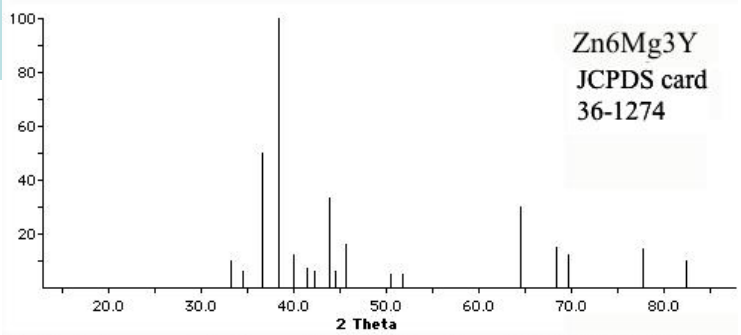
φ-phase corresponds to the icosahedral quasicrystal, but **before Prof. Tsai, nobody realized it.**




Phase diagram of a ternary Al–Cu–Fe system.

Bradley, A. J.; Goldschmidt, H. J. An X-ray study of slowly cooled iron–copper aluminium alloys. Part II. Alloys rich in aluminium. *J. Inst. Met.* **1939**, *65*, 403–418.

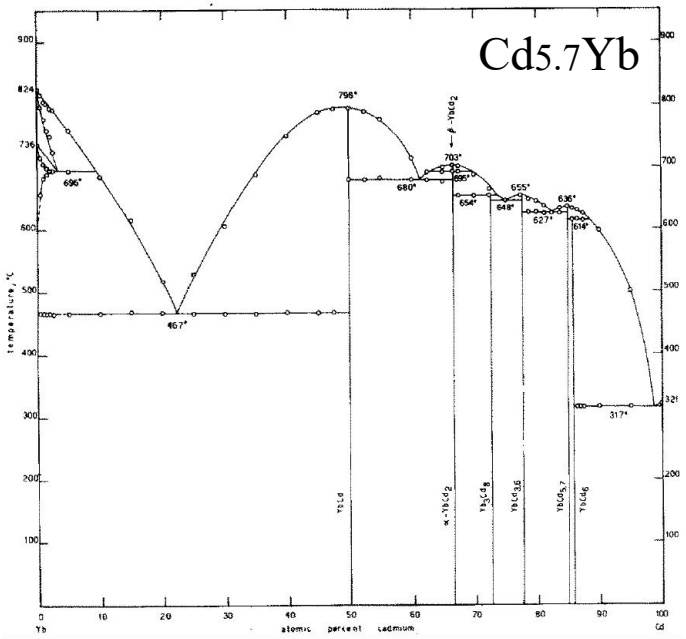
## Zn-Mg-Y




E. Padezhova, et al., Russ. Metall. (Eng. Transl.) 1982 185 (1982).

## Cd-Yb phase diagram

$Cd_{5.7}Yb$ is quasicrystal, but again **nobody noticed except for Prof. Tsai.**




The Ytterbium-Cadmium System, A. Palenzona, J. Less-Common Metals, 25 (1971) 367-372.

# Al-Cu-Fe icosahedral quasicrystal (1987)

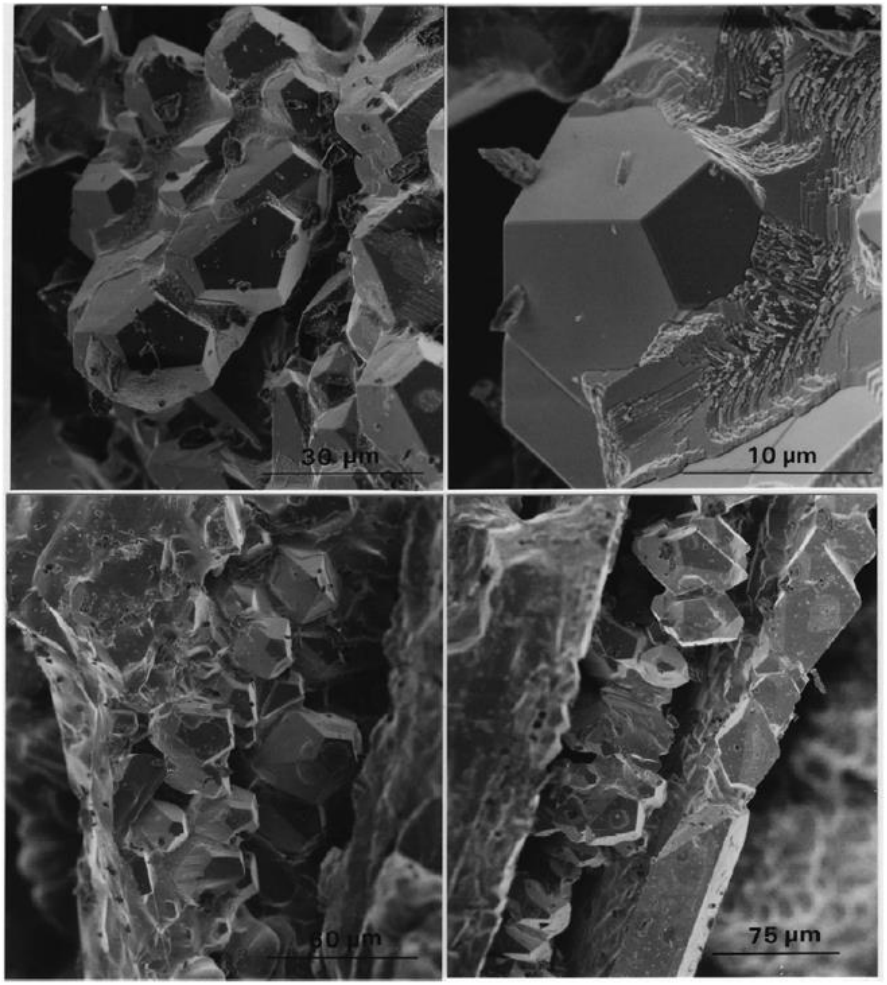



**Fig. 3** SEM images of the $Al_{65}Cu_{20}Fe_{15}$ alloy prepared by arc melting.

**Discovery of stable icosahedral quasicrystals: progress in understanding structure and properties†**

An-Pang Tsai*[ab]

*Chem. Soc. Rev.*, 2013, **42**, 5352–5365

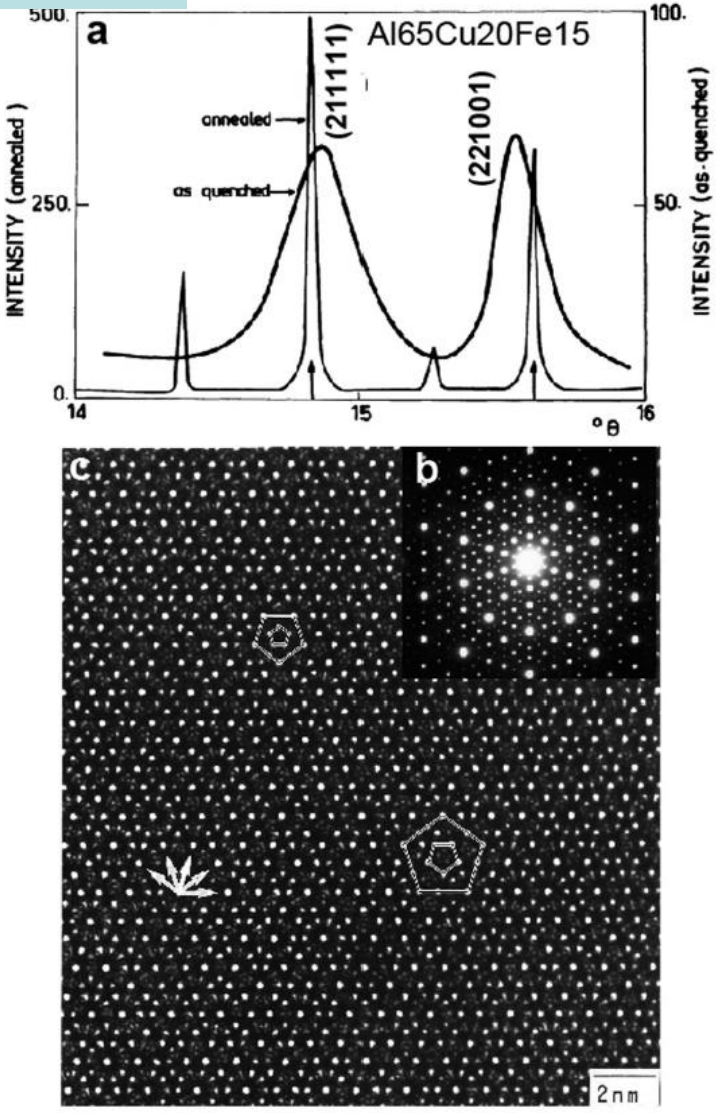



**Fig. 4** (a) Powder X-ray diffraction patterns obtained from the melt-quenched $Al_{65}Cu_{20}Fe_{15}$ alloy under as-quenched conditions and after annealing at 800 °C.[12] (b) Electron diffraction pattern and (c) high-resolution TEM image taken along the five-fold axis of annealed sample (courtesy of M. Terauchi).

# Significance of discovery of stable quasicrystals

1. To improve phase purity
2. To synthesize single crystal
3. To achieve high structural quality

Essential to understand what is a quasicrystal.

Yoshihiko Yokoyama, Tsuneo Miura, An-Pang Tsai, Akihisa Inoue and Tsuyoshi Masumoto

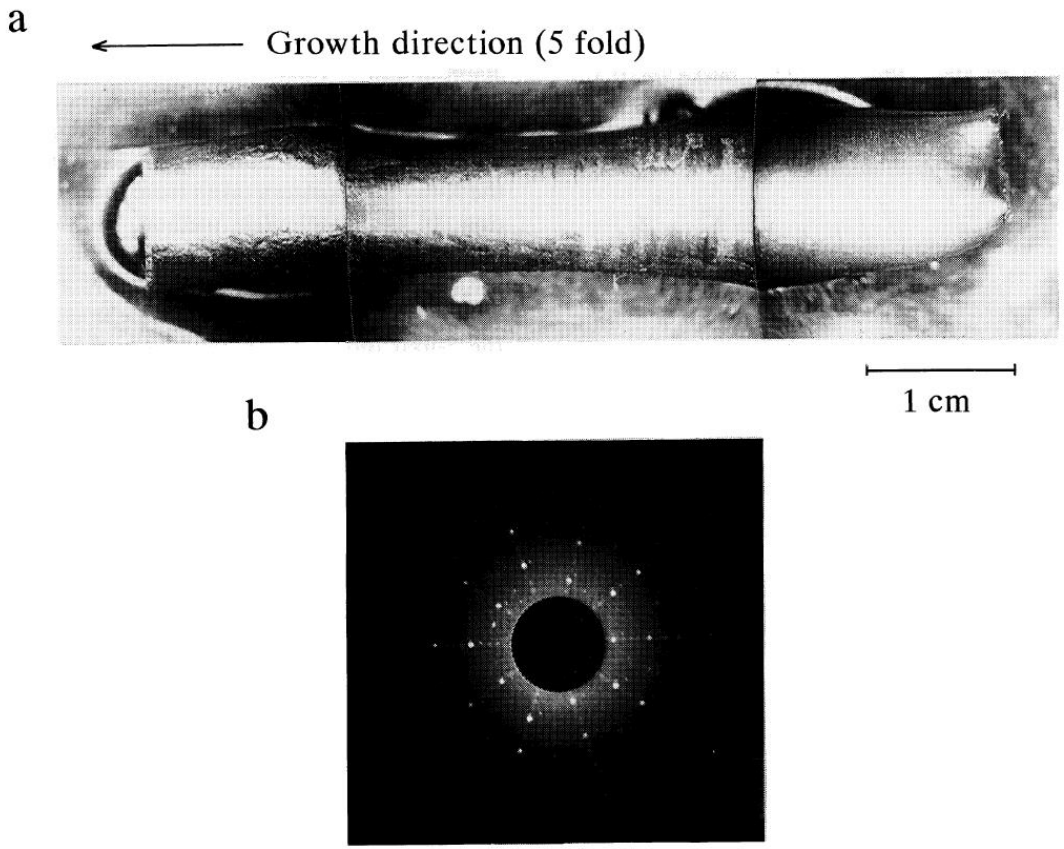



Fig. 7 (a) Outer appearance of an $Al_{70}Pd_{20}Mn_{10}$ single-quasicrystal grown from the seed quasicrystal shown in Fig. 6 by the Czochralski method. (b) X-ray Laue pattern revealing the five-fold symmetry taken from the growth direction.

Al-Pd-Mn single quasicrystal made by Czochralski method (1992)

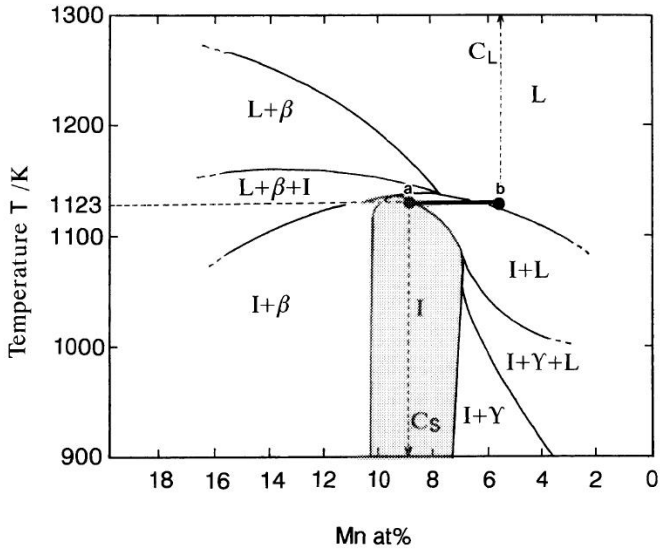



Fig. 2 Equilibrium phase diagram of pseudo-binary $Al_{80-X}Pd_{20}Mn_X$ ($X$: 3 to 15 at%) system. The $C_S$ and $C_L$ represent the compositions of the icosahedral solid and the liquid in equilibrium with the icosahedral solid at 1123 K, respectively. L: liquid, I: icosahedral phase, $\beta$: cubic AlPd, $\gamma$: $Al_3Pd$.

# Cd-Yb Alloys - A stable binary quasicrystal, A.P. Tsai et al., Nature, 408 (2000) 537.

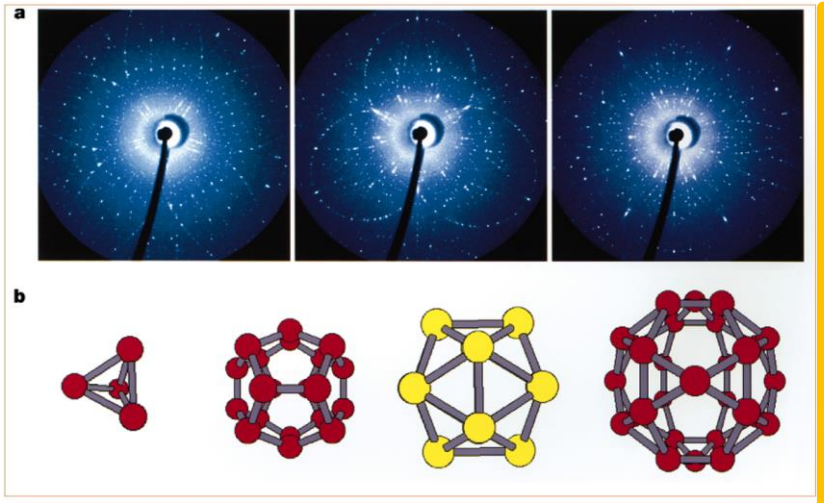
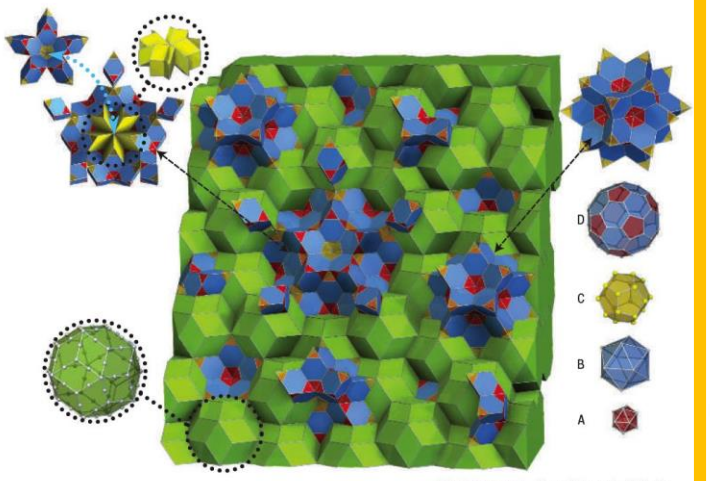



**Figure 1** $Cd_{5.7}Yb$ quasicrystal. **a,** Transmission Laue X-ray diffraction patterns along 5-fold, 3-fold and 2-fold axes (respectively, left to right) from a single quasicrystal. Based on its orientation, the quasicrystal was confirmed to have icosahedral symmetry. Patterns were obtained from a single grain, indicating that the quasicrystal structure is stable enough to create a bulk form. **b,** Decoration of the icosahedral cluster in the quasicrystalline $Cd_{5.7}Yb$ alloy, as deduced from the cubic $Cd_6Yb$ crystalline approximant. The first shell is created by four Cd atoms around the cluster centre, the second consists of 20 atoms forming a dodecahedron, the third is an icosahedron of 12 Yb atoms, and the fourth is a Cd icosidodecahedron obtained by placing 30 Cd atoms on the edges of the Yb icosahedron. In all, the icosahedral cluster consists of 66 atoms. Cd, red atoms; Yb, yellow atoms.

ARTICLES




H. Takakura et al., Nature Mater. 6, 2007, 58.

D. Kawana, T. Watanuki, A. Machida,
T. Shobu, K. Aoki and A.-P. Tsai

PHYSICAL REVIEW B **81**, 220202(R) (2010)

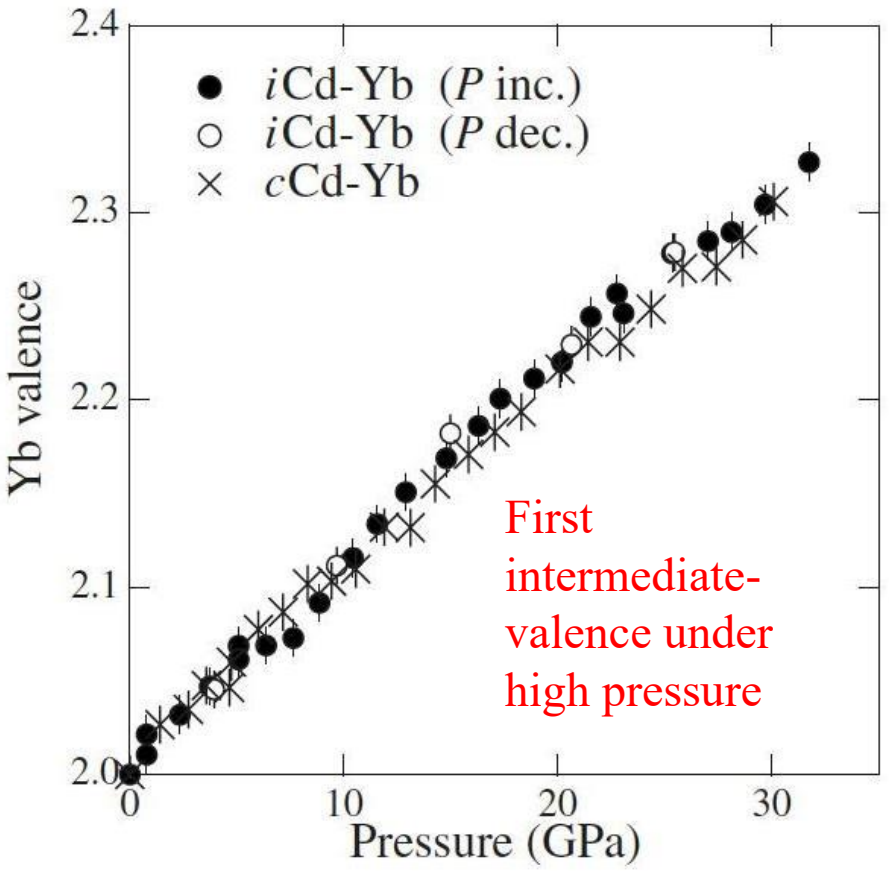



FIG. 2. Pressure dependence of Yb valence in an icosahedral Cd-Yb quasicrystal (*i*Cd-Yb) with compression (closed circles) and decompression (open circles) processes. Results of the crystalline approximant $Cd_6Yb$(*c*Cd-Yb) are also shown (crosses).

# Hume-Rothery rules

## 1. Valence-electron concentration

Matching between Fermi surface and Brillouin zone or Jones zone

## 2. Atomic size factor

## 3. Electronegativity

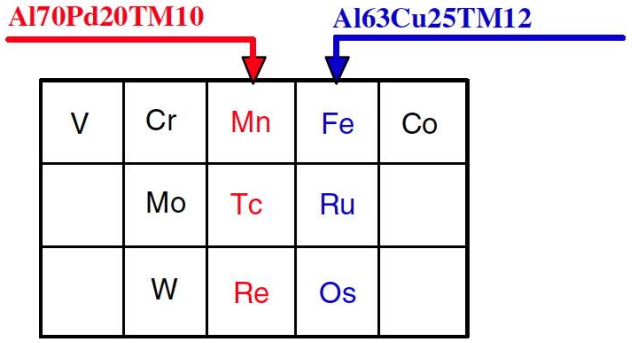



Fig. 1. Formation of stable quasicrystals in Al–Cu–TM and Al–Pd–TM systems, where TM is the transition metal.

*A.-P. Tsai / Journal of Non-Crystalline Solids 334&335 (2004) 317–322*

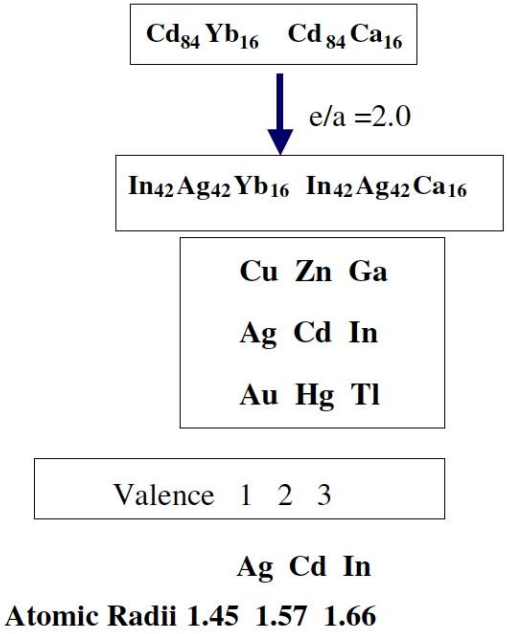



Fig. 2. Formation of stable quasicrystals in Cd binary alloys and Ag–In ternary alloys. *A.-P. Tsai / Journal of Non-Crystalline Solids 334&335 (2004) 317–322*

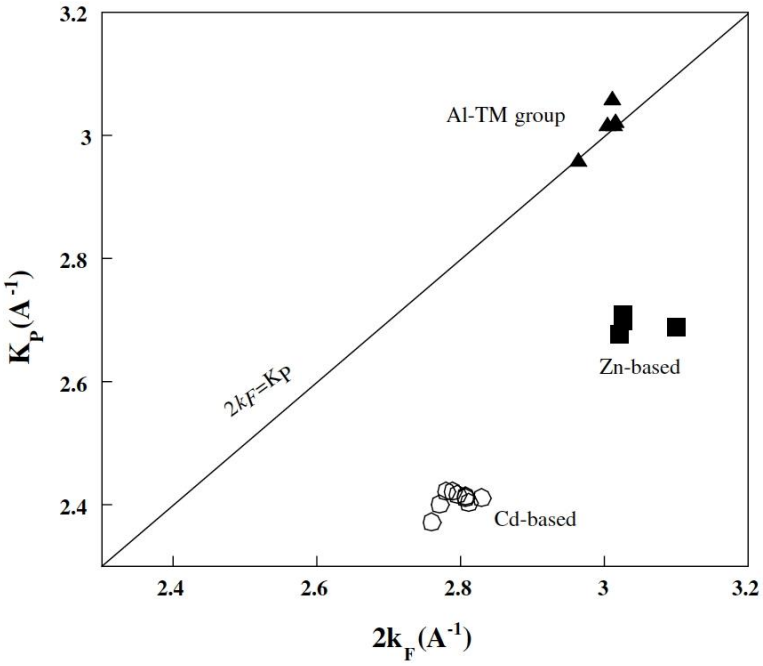



Fig. 3. Relationship of $K_P$ and $k_F$ for stable quasicrystal forming alloys.

*A.-P. Tsai / Journal of Non-Crystalline Solids 334&335 (2004) 317–322*

# Unforgettable contribution to quasicrystal society in Japan

## Prof. Tsai had organized annual meeting on quasicrystals more than 20 years.

5th 1996.12.16-18 (H.9)
NRIM(金属材料技術研究所), Tsukuba, Ibaraki
6th 1997.12.18-20 (H.10)
Nara Women's University, Nara
35 presentations
7th 1999.6.16-18 (H.12)
Tohoku University (金研), Sendai
48 presentations
8th 2000.5.31-6.2 (H.13)
Nagoya University, Nagoya
55 presentations
9th 2002.5.15-17 (H.15)
NIMS, Tsukuba, Ibaraki
44 presentations
10th 2003.10.8-10 (H.16)
Sponsored by JST-CREST
Hokkaido University, Sapporo
52 presentations
11th 2005.12.12-14 (H.17)
Subtitle: Recent developments in quasicrystal research
University of Tokyo/Institute for solid state physics
42 presentations, Opening remarks: K. Uyeda
12th 2007.12.19-21 (H.19)
Tohoku University (多元研), Sendai
35 presentations, Opening remarks: A.Yamamoto
13th 2008.12.15-17 (H.20)
Zuisenkaku (瑞泉閣), Ichinoseki, Iwate
37 presentations
14th 2009.12.17-19 (H.21)
Laforet Zao Hotels & Resort, Zao, Miyagi
37 presentations, Opening remarks: A.P. Tsai
15th 2010.12.13-15 (H.22)
Laforet Zao Hotels & Resort, Zao, Miyagi
29 presentations, Opening remarks: A.P. Tsai

16th 2011.12.14-16 (H.23)
Hokkaido University, Sapporo
33 presentations, Opening remarks: A.P. Tsai
17th 2012.12.19-21 (H.24)
Kinki University, HigashiOsaka
36 presentations, Opening remarks: T. Dotera
18th 2013.12.16-18 (H.25)
Tokyo University of Science, Katsushika, Tokyo
42 presentations, Opening remarks: A.P. Tsai
19th 2014.12.21-23 (H.26)
Laforet Zao Hotels & Resort, Zao, Miyagi
37 presentations, Opening remarks: A.P. Tsai

20th 2015.12.17-19 (H.27)
Tokyo University of Science, Katsushika, Tokyo
37 presentations, Opening remarks: A.P. Tsai
21st 2017.3.2-4 (H.29)
Hokkaido University, Sapporo
35 presentations, Opening remarks: A.P. Tsai
22nd 2018.3.5-6 (H.30)
Tohoku University (TOKYO ELECTRON House ), Sendai
26 presentations, Opening remarks: A.P. Tsai
23rd 2018.12.18-19 (H.30)
Tokyo University of Science, Katsushika, Tokyo
30 presentations, Opening remarks: A.P. Tsai

# E-mail from Prof. Tsai dated 15 Oct 2003 after the meeting in Sapporo

Date: Wed, 15 Oct 2003 10:22:39 +0900
To: ishimasa@eng.hokudai.ac.jp (Tsutomu Ishimasa)
From: An Pang Tsai <aptsai@quasi.nims.go.jp>
Subject: Re: 受け付け
Status:

石政先生

今回は石政さんの全面的なご協力を得て、今回の準結晶研究会が大成功に終わりました。ありがとうございます。
柏本君をはじめ、研究室の学生さんにお礼を申し上げます。宜しくお伝え下さい。
天候に恵まれて、参加者全員は北海道の秋風景と海の幸を楽しんできたことに違いありません。私もほぼ一週間、続けて飲んできました。恐らく、石政さんにも体が疲れ果てたのではないかと想像しています。お疲れさまでした。
今回の研究会において特筆すべきのは若手の方々の質問などが目立っており、いままで最も活気のある研究会すら思わせるほどの熱い研究会でした。準結晶研究の将来に明るい兆が見えてきたと思います。この勢いで来年の台湾のワークショップに乗り込みたいものですね。
簡単ながらお礼とさせていただきます。

また、石政先生の方で、消耗品などが必要があれば、気軽に申し付けてください。研究に支障がないように、協力したいと思います。

重ねてお礼を申し上げます。

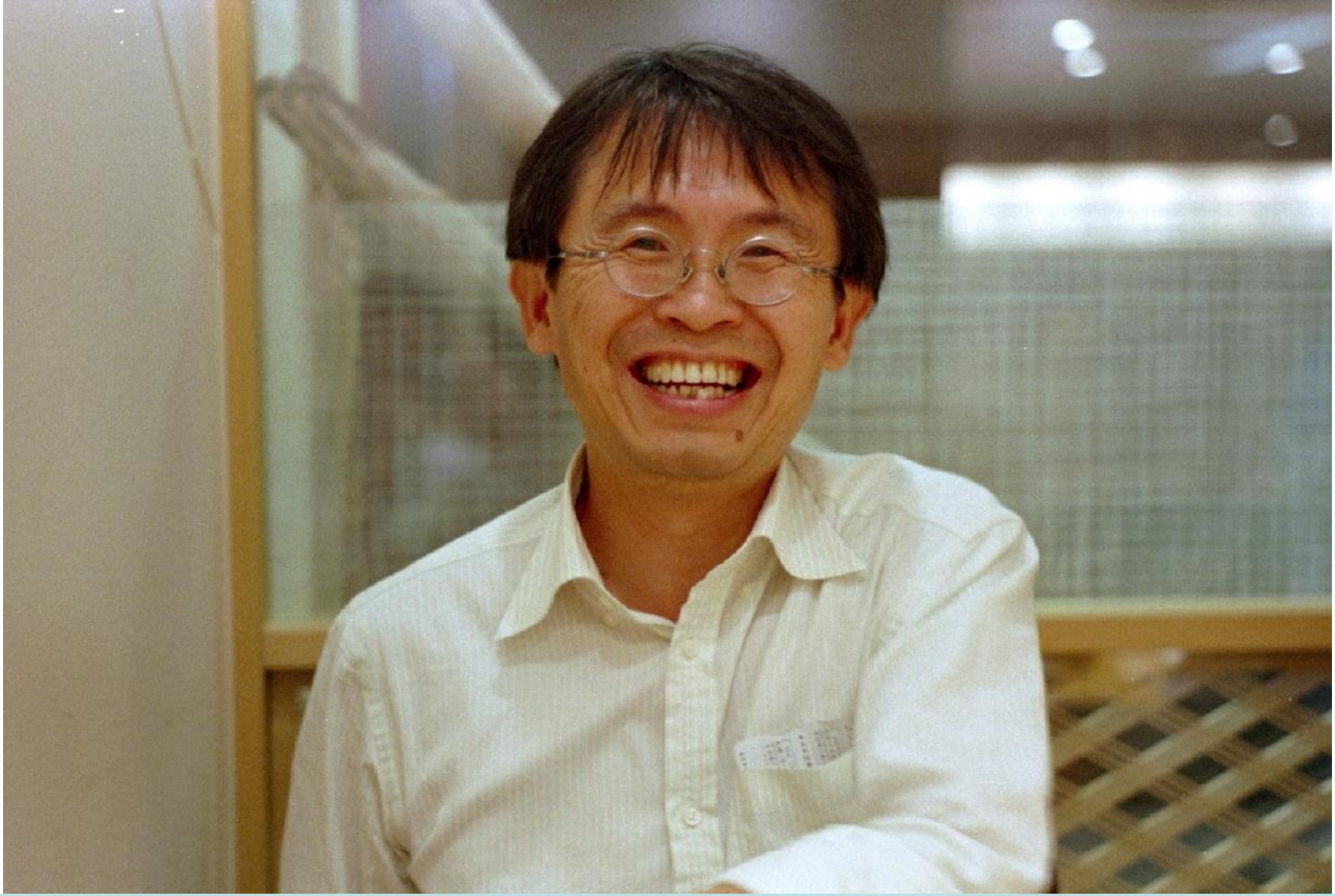
蔡

Professor Ishimasa

This time with the full cooperation of Mr. Ishimasa, this quasicrystal study meeting ended in great success.
Thank you very much.
I would like to thank Mr. Kashimoto and the students in the laboratory. Please tell my thanks.Blessed with the weather, it is sure that all the participants enjoyed the autumn scenery and seafood of Hokkaido.I had also been drinking too much for almost a week. I imagine that your body is tired too.
It is noteworthy at this meeting that the young people's questions were outstandingly. It was so active that even the most lively meeting was reminiscent. I think that bright signs in future of quasicrystal research have been seen.
I would like to board a workshop in Taiwan next year with the same passion.

Also, if you needs expendable supplies, please feel free to tell me.
I would like to cooperate so that there is no hindrance to research.

Thank you again.
Tsai



We lost very best teacher, and very best friend at the same time.
We pray that his soul may rest in peace.